



Metal phosphate catalyzed dehydration of sorbitol under hydrothermal conditions

Oana Alice Rusu^{a,c}, Wolfgang F. Hoelderich^{a,d,*}, Hervé Wyart^b, Mathias Ibert^b

^a Formerly Department of Chemical Technology and Heterogeneous Catalysis, RWTH Aachen University, Worringerweg 1, D-52074 Aachen, Germany

^b Roquette Frères, 1 Rue de la Haute Loge 62136 Lestrem, France

^c Institute for Nuclear Research Pitesti, Campului 1 Str., P.O.B. 78, 115400, Mioveni, Romania

^d TCHK Hoelderich Consultancy, D 67227 Frankenthal, Germany

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ABSTRACT

The intention of this work is to develop a heterogeneously catalyzed, environmentally friendly and sustainable process for the production of isosorbide by dehydration of sorbitol. The presence of the heterogeneous catalyst BP in the batch reactor had a great influence on the reaction rate. Trivalent B-, Al-, Fe-, Ce- and La-phosphates catalysts (MeP), as well as quadrivalent Zr-phosphates (ZrP-1 and ZrP-2) were studied in liquid-phase using autoclave reactors under autogenous pressure at different temperatures between 150 and 250 °C for different reaction times between 0.5 and 24 h. The catalytic activity depends on the acidity of the catalysts, as NH₃-TPD technique revealed, on the surface area and the pore diameter determined by N₂ adsorption. Depending on the pH of the reaction medium, water molecules play a significant role in the reaction. A tremendous effect was observed when 100 wt.% sorbitol powder was used instead of aqueous 70 wt.% sorbitol solution as starting material.

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1. Introduction

Isosorbide belongs to the so-called “biomass-derived substances”, obtainable from natural products, being classified as “renewable resources”. This 1,4:3,6-di-anhydrohexitol is useful in the formation of numerous pharmaceutical compounds, cosmetics, products of food industry [1], as well as polymers such as polyurethane, polycarbonate, polyesters and polyamides [2,3].

An overview on catalytic sorbitol dehydration investigation has been provided by Li et al. [4], in which three research groups considering the phases of catalysts and reactants are identified. The first group claims the classic way whereby water is used as solvent for both catalysts based mineral acids and reactant [5–10]. Among the strong mineral acids (H₂SO₄, H₃PO₄, HCl) H₂SO₄ seems to be the best under the same conditions (100% sorbitol conversion and 77% isosorbide yield at 135 °C, 20 h) [10].

Recently, following a new strategy, molten ZnCl₂ hydrate is applied as solvent as well as catalyst. Thereby full conversion of

sorbitol and high selectivity to isosorbide (>85% on molar basis) were achieved at 200 °C [4]. But besides the high pressure conditions (30 bars N₂) needed, this method presents drawbacks like all the others homogeneously catalyzed processes e.g., solvent recycle, strong salt formation [11].

The second and the third group presented more environmentally friendly and sustainable attempts by applying heterogeneous catalysts. These catalysts can be easily removed and recovered from reaction mixtures, and thus, can be used several times. Furthermore, the strong salt formation due to the neutralization of the homogeneous acid is strongly reduced and the usage of solvents and environmentally adverse chemicals are prevented [12,13]. When solid acid catalysts are used the fed sorbitol can be solid (second group, sorbitol melting point is 95 °C) or in an aqueous solution (third group).

Researchers focused on the study of using H-zeolites [14,15], SiO₂–Al₂O₃ [16], ion-exchange resins [10,17], H₃PW₁₂O₄₀/SiO₂ [18], anhydrous pyridinium chloride [19] and bimetallic catalysts (Cu–Pt, RANEY copper, acid promoted Pt) [20]. Acceptable yields of isosorbide (62% [16] and 81% [15]) were obtained in the presence of SiO₂–Al₂O₃ [16] and 3 Å zeolites [15], but only at elevated temperatures and pressures. Furthermore, the zeolites have the disadvantages of being expensive catalysts.

Due to the low activity and poor selectivity of classic solid acid catalysts such as silica, alumina the development of more efficient

* Corresponding author at: Formerly Department of Chemical Technology and Heterogeneous Catalysis, RWTH Aachen University, Worringerweg 1, D-52074 Aachen, Germany. Present TCHK Hoelderich Consultancy, D 67227 Frankenthal, Germany.

E-mail address: hoelderich@rwth-aachen.de (W.F. Hoelderich).

solid acid catalysts has been investigated. For instance, a maximum of 75% selectivity to isosorbide, with 100% conversion of sorbitol is achieved over sulfated titania at 210 °C [21].

Al-Qallaf et al. [22] described good performances of metal(IV) phosphates for selective formation of mono- and bi-cyclic ethers from diols. Metal(IV) oxides modified with H₃PO₄ [23] and metal(IV) phosphates, as tin, zirconium and titanium phosphates [24,25] were tested for selective dehydration of sorbitol to isosorbide in gas-phase. Among these quadrovalent metal phosphates tin phosphate showed the highest selectivity to isosorbide (65.4%) but with moderate sorbitol conversion (72.1%) [25]. However, these quadrovalent phosphates present the inconvenience to be expensive, because their preparation requires a sequence of energy consuming subsequent processes, e.g., calcinations, refluxing for long times, hydrothermal treatment. More than that, some of them are toxic, such the tin phosphate [26].

In recent years increasing interest has been focused on trivalent cations containing phosphates used as catalysts in organic synthesis and in petrochemical industry [27]. The Me(III) phosphates are cheaper catalysts than quadrovalent phosphate catalysts. They can be easily prepared, just by mixing together a soluble source of the trivalent metal cation and a source of the phosphate anion [28].

Sorbitol dehydration at high temperature liquid water (200–300 °C, without using any catalyst) was recently reported by Yamaguchi et al. [29], with a maximum yield of isosorbide of 55% after 3 h at 300 °C.

The objective of the present work is to develop a simple, low cost, environmentally friendly and sustainable process for the production of isosorbide by dehydration of sorbitol. Therefore this study describes investigations of the reaction carried out in liquid-phase over B-, Al-, Fe- Ce- and La- trivalent cations containing phosphates as well as the quadrovalent Zr- phosphates as catalysts under hydrothermal conditions. Although the effect of water on the dehydration of sorbitol is well known and that by continuously removing the water from the system the rate of isosorbide synthesis increases 5 times [10], in the last years the reaction has been studied in closed systems, as the batch reactors with [4] and without catalyst [29] and good results have been reported. Therefore, for comparison reasons in this paper only experiments in closed autoclaves without water separation have been carried out.

2. Experimental

2.1. Catalysts

Different metal phosphates have been studied as catalysts for sorbitol dehydration: boron phosphate (BP, kindly provided by BASF), aluminum phosphate (AlP, AlPO₄, CAS: 7784–30–7, bought from ABCR), two different zirconium phosphates (ZrP-1 (NZP 100) and ZrP-2 (CZP-200), both kindly sponsored by MEL), iron phosphate (FeP, FePO₄·4H₂O, CAS: 31,096–47–6, bought from Fluka), lanthanum phosphate (LaP, [28,30]) and cerium phosphate (CeP, [28,30]). All these catalysts were used in the reaction as provided or as prepared or after calcination in air. BP, ZrP-1, ZrP-2 and CeP were calcined using 3 different treatments: at 200 °C for 12 h (denoted MeP²⁰⁰), at 400 °C for 8 h (denoted MeP⁴⁰⁰) and at 600 °C for 12 h (denoted MeP⁶⁰⁰).

2.2. Characterization of the catalysts

X-ray diffraction (XRD) analysis was performed on a Siemens D 500 diffractometer using CuK α monochromatized radiation source operated at 40 kV and 40 mA. The BET surface area and BJH pore volumes were calculated from nitrogen adsorption/desorption at 77 K using Micromeritics ASAP 2000 instrument. NH₃-TPD was

carried out with the POROTEC TPDRO 1100 instrument equipped with a thermal conductivity detector. XPS measurements were performed on a Thermo Scientific ESCALAB 250 electron spectrometer equipped with aluminum anode using the monochromatized AlK α radiation ($h\nu$ = 1486.6 eV) from an anode operated at 15 kV and 150 W. The elemental analysis was done by Inductively Coupled Plasma atomic emission spectrometry (ICP-AES) by a Spectroflame Modula FTM18 of Spectro Analytic Instrument using two monochromators in the wavelength ranges of 165–460 and 240–790 nm, respectively.

2.3. Batch reaction procedure

The batch experiments were carried out in 75 ml stainless steel autoclaves equipped with pressure gauges. The autoclave was heated up to the reaction temperature by means of an electrical heater jacket equipped with a temperature controller. The stirring was achieved using a magnetic stirring bar inside the reaction mixture. An aqueous solution with 70 wt.% sorbitol was used as reactant as well as a 100 wt.% powder (both kindly supplied by Roquette Frères, Lestrem, France). Two different amounts of reactants were tested: 25 ml/50 ml in the case of sorbitol solution and 32.3 g/45.5 g in the case of sorbitol powder, respectively. The catalyst weight was in each reaction 1 wt.% related to the amount of the sorbitol (0.32 g and 0.46 g). The autoclave was sealed and heated up to the chosen temperature and for the specified reaction time under an adjusted stirring speed (1100 rpm) and self-generated pressure. In one experiment the system was artificially pressurized to 20 bars with nitrogen gas prior to heating. After the given reaction time, the heating device was removed and the autoclave was cooled down to room temperature by immersing into an ice bath. Six different temperatures were adjusted at 150, 180, 190, 200, 220 and 250 °C for different reaction times of 0.5, 1, 2, 4, 8, 12 and 24 h.

2.4. Gas chromatography

The gas chromatographic analysis was performed on a Hewlett Packard HP 6890 Series GC system, using a capillary column FS-OV-1-CB, CS25208-1 (50 m \times 0.25 μ m \times 0.25 μ m). The temperature program of the column was: 140 °C, 2°/min, 250 °C. The injected volume was: 1 μ l.

The GC samples were prepared as follows. Around 100 mg of sample (the mixture obtained at the end of the reaction) was solved in 1 ml pyridine. This solution was called 'concentrated solution'. A big volume of a solution of ethylene glycol (used as internal standard, IS) was prepared as follows: 3.1214 g of ethylene glycol were solved in 50 ml pyridine. From this solution 0.67 ml were taken for each analysis. These 0.67 ml of IS solution were mixed with 2 ml of *N,O*-bis(trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane (BSTFA + 1% TMCS, reagent for trimethylsilylation). This new solution was called 'silylation solution'. 0.1 ml of 'concentrated solution' was mixed with 0.8 ml of 'silylation solution'. The mixing process was performed in ultrasound bath for 30 min. So, for silylation of the sample it was used the following rapport: 6 mg sample/5 mg IS/2 ml BSTFA.

For the calculations of conversion and selectivities the total mass of the sample analyzed was considered equal with the initial mass of the reactant. The conversion of sorbitol was determined from the percentage of transformed sorbitol (sorbitol initial – sorbitol in the sample).

$$X_{\text{SORBITOL}} = \frac{m_{\text{SORBITOL INITIAL}} - \%_{\text{SORBITOL}}/100 \times m_{\text{TOTAL SAMPLE}}}{m_{\text{SORBITOL INITIAL}}} \times 100, \text{ where}$$

X_{SORBITOL} is conversion of sorbitol, % mol, $m_{\text{SORBITOL INITIAL}}$ is the initial mass of sorbitol, g, $\%_{\text{SORBITOL}}$ is the % of sorbitol determined by GC in the sample analyzed,

Table 1

Crystalline phases of metal phosphates determined by XRD.

Catalyst	Crystalline phases
BP	BPO ₄
AlP	AlPO ₄ syn. berlinite and AlPO ₄
ZrP-1 (NZP-100)	(H ₃ O)Zr ₂ (PO ₄) ₃
ZrP-2 (CZP-200)	Zr(PO ₄)(H ₂ PO ₄)(H ₂ O) ₂
FeP	Amorphous
LeP	Amorphous
CeP	Amorphous

$m_{\text{TOTAL SAMPLE}}$ is the total mass of the sample analyzed, g.

The selectivity of the product i represents the molar percentage of the product obtained by dividing the molar amount of product i by the molar amount of transformed sorbitol.

$$S_i = \frac{\%i/100 \times m_{\text{TOTAL SAMPLE}}/M_i}{X_{\text{SORBITOL}}/100 \times m_{\text{SORBITOL INITIAL}}/M_{\text{SORBITOL}}} \times 100 \text{ where,}$$

S_i is the selectivity of product i , % mol, M_i is the molecular mass of the product i , M_{SORBITOL} is the molecular mass of sorbitol.

3. Results and discussion

3.1. Characterization of catalysts

X-ray diffraction technique has been used to study the structures of the metal phosphates. The crystallization phases attributed to these solids are presented in Table 1. By calcination at temperatures in the range 200–600 °C BP preserves its crystallinity, as it is shown in Fig. 1. The lines are only slightly sharper, of BP⁴⁰⁰ more than BP⁶⁰⁰.

Table 2 illustrates the BET surface and the pore size distribution for the investigated metal phosphates obtained by the N₂ adsorption–desorption data by means of an ASAP 2000 instrument. The differences between the physical features of the uncalcined and calcined BP catalysts are more evident when the calcination temperatures are higher than 200 °C. An important change in pores size happened when BP has been calcined at 600 °C. It was shown that the surface area of BP increases with pretreatment temperature up to the maximum temperature (450 °C), and afterwards decreases [31,32]. The increase of the total pore volume and of the average pore radius with pretreatment temperature has been reported [33], but in our case this happened up to 400 °C; but in our case higher temperatures result in a decrease of both surface properties. Mof-

fat and Goltz [31] presumed that the increase in surface area on heating may be due to the evolution of water from the bulk of the solid during the heating and evacuation process. The transfer of this water from the interior to the surface of the solid could lead to the production of additional porous structure. They presume that all the entrapped water escape between 200 and 300 °C and by further increase of temperature by collapse of some of the pores may occur, resulting in a decrease in surface area.

NH₃-TPD measurements were performed to determine qualitatively the acid strength on catalyst surface of the investigated metal phosphates as depicted in Fig. 2. Desorption peaks with maxima in the range 100–200 °C, 200–400 °C, 400–600 °C in the NH₃-TPD pattern are commonly attributed to NH₃ that has been chemisorbed on weak, medium and strong acid sites, respectively [34]. Some solids present strong acid sites which desorb the chemisorbed NH₃ at temperatures higher than 600 °C [35]. Peaks with maximum around 850 °C can be identified in case of some phosphates studied in this work and these give a hint of the presence of excessively strong acid sites. The total acid amount and the amount of every type of acid sites can be determined by integrating the TPD curve and the TPD peaks individually, respectively. As it can be realized in Fig. 2 BP has a broad range of acid sites with various strength, while AlP has very low acidic sites with low strength. Concerning the acidic strength all samples showed typically three desorption peaks with the maxima at 180 °C, around 550 °C, 800 °C and 850 °C denoted as weak, strong, very strong and excessively strong acid strength. BP has a large section of acid sites, larger than the other phosphates. The wide range in case of BP reveals medium acid strength sites with the maximum at 400 °C, strong acidic sites with the maximum at 550 °C and very strong acidic sites with the maximum at 750 °C.

The NH₃-TPD profiles of BP calcined at three different temperatures compared with the NH₃-TPD profile of uncalcined BP show, that the calcination at 200 °C (BP²⁰⁰) almost preserves the acidity of uncalcined BP, while the calcination at 400 °C (BP⁴⁰⁰) and 600 °C (BP⁶⁰⁰) result in decreased acidity, but stronger (the TPD curve exhibits a rightward deviation). For BP calcined at 200 °C the NH₃ desorption temperature is at around 600 °C and for calcination at 600 °C at around 900 °C. That means the higher the calcination temperature the higher the acidic strength. On the other hand, the increase in very strong and excessively strong acidity by elevated calcination temperatures is accompanied by the decrease of moderate and strong acidity. It was reported that all pretreatment temperatures from 200 to 600 °C increase the concentration of acid

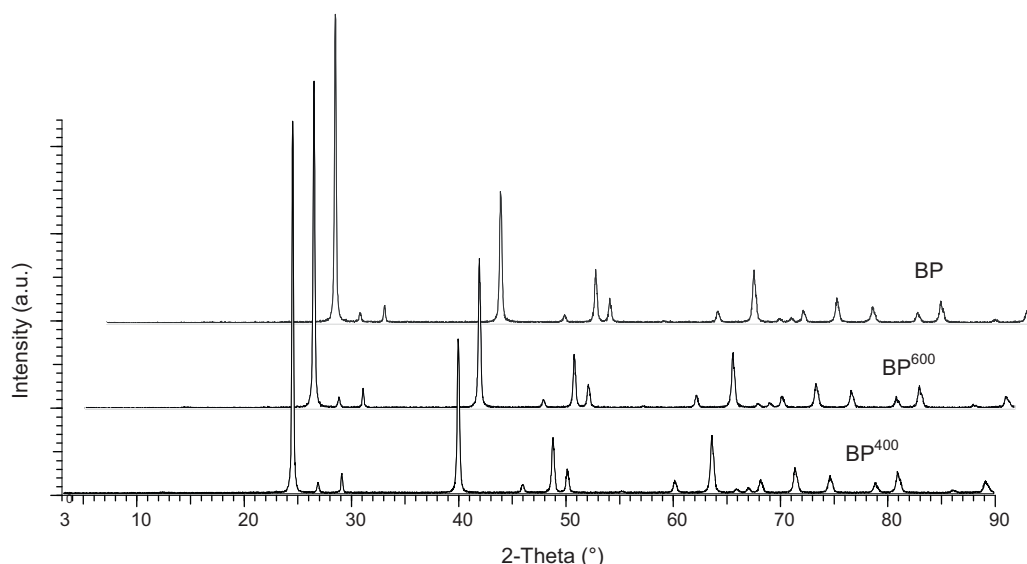


Fig. 1. XRD of BP and the calcined forms, BP⁴⁰⁰ and BP⁶⁰⁰.

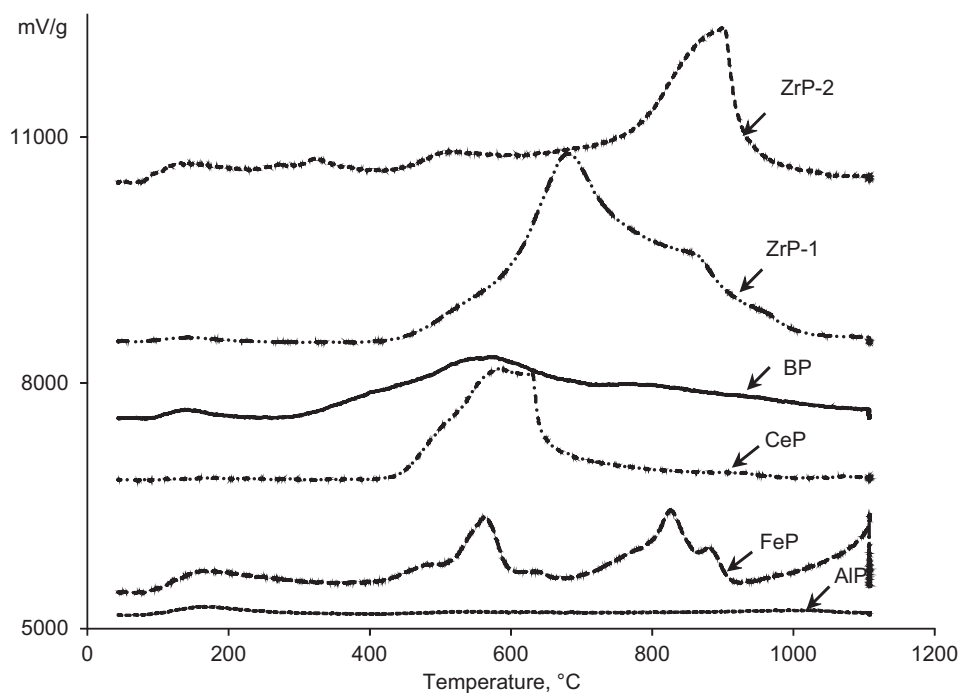


Fig. 2. NH_3 -TPD profiles of metal phosphates.

Table 2

Data from adsorption–desorption of N_2 .

Catalyst	BET surface area (m^2/g)	BJH pore volume of pores between 10 and 500 Å radius (cm^3/g)	BJH average pore radius (Å)
AlP	6.3 ± 0.04	0.02	87.98
ZrP-1	4.1 ± 0.04	0.01	63.21
ZrP-2	15.88 ± 0.21	0.06	107.84
FeP	31.64 ± 0.13	0.11	88.63
CeP	10.57 ± 0.05	0.04	62.22
BP	8.45 ± 0.09	0.06	150.66
BP ²⁰⁰	7.5 ± 0.04	0.05	148.8
BP ⁴⁰⁰	9.6 ± 0.05	0.07	142.2
BP ⁶⁰⁰	6.1 ± 0.04	0.02	105.9

sites of strength $H_0 \leq -3.0$ on BP with P/B ratio of 1.2 [36] and pretreatment at 600 °C generates the strongest acid sites in BP [37].

Relevant spectra of La 3d and Ce 3d photoemission lines are illustrated in Fig. 3. The whole set of spectra undergoes a shift due to a well-known charging effect, which induces a broadening of the peak. C 1s emission peak arises from hydrocarbon contamination and its binding energy is generally accepted as remaining constant, irrespective of the chemical state of the sample. The theoretical position of the C 1s emission, at 284.9 ± 0.1 eV [38], was used as a reference for all charge shift corrections. The average binding energy values of the 3d lines ($3d_{3/2}$ at 851 eV and $3d_{5/2}$ at 835 eV) of the LaP sample are in good agreement with those reported elsewhere for La(III) oxidation state [39,40]. The strong Ce 3d signals ($3d_{3/2}$ at 903.9 eV and $3d_{5/2}$ at 885.2 eV) observed are characteristic for cerium atoms in the 3+ oxidation state [40,41]. The well-defined structure (916.8 eV) observed for Ce(IV) in CeO_2 is not very visible in our Ce 3d spectra, this fact enables us to conclude that the Ce(III) oxidation state is strongly predominant in the sample CeP.

3.2. Catalytic dehydration of sorbitol to isosorbide

3.2.1. Product distribution and the reaction pathway

A careful analysis of the product mixtures obtained at different temperatures and reaction times was made by GC chromatography. Fig. 4 illustrates a summary of these results. Two different

steps have been identified. After 30 min reaction time four significant peaks of monoanhydrohexitols reach a maximum. With respect to their retention time in the GC-column they are denoted MAH V (the more significant), MAH I, MAH II and MAH IV. By gas-chromatography calibration, MAH V was assigned to 1,4-anhydrosorbitol – denoted in the paper 1,4 sorbitan. Simultaneously, 1,4-anhydrosorbitol and MAH IV show a decrease in concentration (Fig. 4a and c), while MAH I and MAH II, present a plateau (Fig. 4b). With the decrease of 1,4-anhydrosorbitol and MAH IV, the isosorbide is increasing. The distribution revealed ahead is registered at temperatures between 180 and 220 °C. At 250 °C, MAH IV is formed in traces and MAH I and MAH II show a decline, caused probably by polymer formation.

Isomers of isosorbide are formed in traces. Isosorbide is formed at temperatures higher than 200 °C and isomannide at temperatures lower than 200 °C. It is generally agreed that sorbitol dehydration into isosorbide takes place through the intermediates 1,4- and 3,6-monoanhydrosorbitols, whereas the commonly observed isomers 1,5- and 2,5-monoanhydrohexitols are stable under those reaction conditions. The similar behavior was revealed by Li et al. [4] when they studied the sorbitol conversion in aqueous 70 wt.% ZnCl_2 in a batch titanium autoclave and by Yamaguchi et al. when they studied the reaction in high temperature liquid water [29]. Comparing our results with those reported in the literature [4,29] and taking into account the molecular modeling study of sorbitol dehydration [42] we come to the conclusion that MAH IV

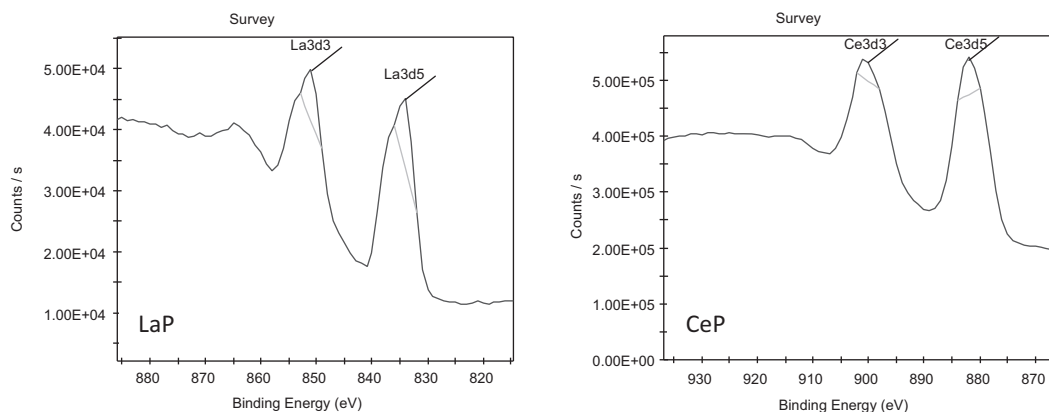


Fig. 3. The XPS of LaP (left) and CeP (right) in the La 3d and Ce 3d binding energy regions.

is 3,6-anhydrosorbitol, MAH I 1,5-anhydrosorbitol and MAH II 2,5-anhydrosorbitol.

There were traces of a product P, the first one separated in the GC column. From its distribution over time (Fig. 4d) we can conclude that it is a volatile product. The other 4 MAHs are formed in traces. The product P is not taken into account in the present discussion. There is not any evidence of isomerization of sorbitol into galactitol, as it was found in the case of ZnCl_2 molten salt hydrate medium [4]. The product distribution indicates a rather simple pathway for the isosorbide formation, like as it is proposed in the reaction scheme (Scheme 1).

In the first dehydration step two types of monoanhydrosorbitols are formed; the first type (1,4- and 3,6-anhydrosorbitol) reacts sequentially to isosorbide and the second type (1,5- and 2,5-anhydrosorbitol) is stable towards further dehydration. Isomerization of isosorbide into isoidide and isommanide is also included in the reaction pathway. The fact that there is no evidence for galactitol formation, the pathway proposed is simpler than that given by Li et al. [4]. In this paper the results are discussed also from the point

of view of the sum isosorbide + 1,4 sorbitan, denoted “isosorbide potential” of the catalyst. After separation of the catalyst the reaction mixture was also checked for B content by means of ICP-AES. No traces of B could be detected. That means no leaching took place.

3.2.2. Effect of reaction conditions

To investigate the effect of the reaction temperature on the conversion of sorbitol (70 wt.% aqueous sorbitol solution) the reactions were carried out in the temperatures range from 150 to 250 °C as illustrated in Table 3. Some of the experiments have been reproduced but there was no difference observed. Almost complete conversion of sorbitol is found in all the cases. At 180 °C the conversion is 96.4% and at higher temperatures it reaches 99–100%. If the isosorbide potential does not widely vary with temperature, i.e., around 75–80%, its selectivity gradually increases to these values with temperature increased over 200 °C.

Gu et al. [25] had investigated the influence of reaction time on sorbitol conversion over TiPO , SnPO and ZrPO at 300 °C in gas phase. In the first 12 h the sorbitol conversion declined for all catalysts

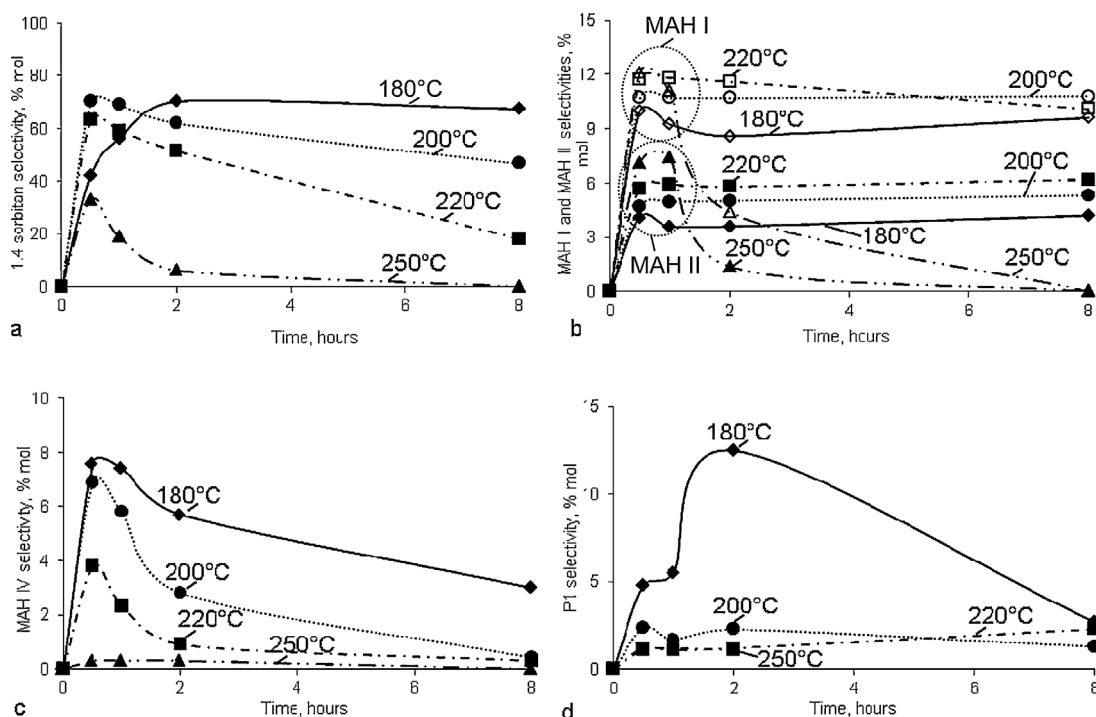
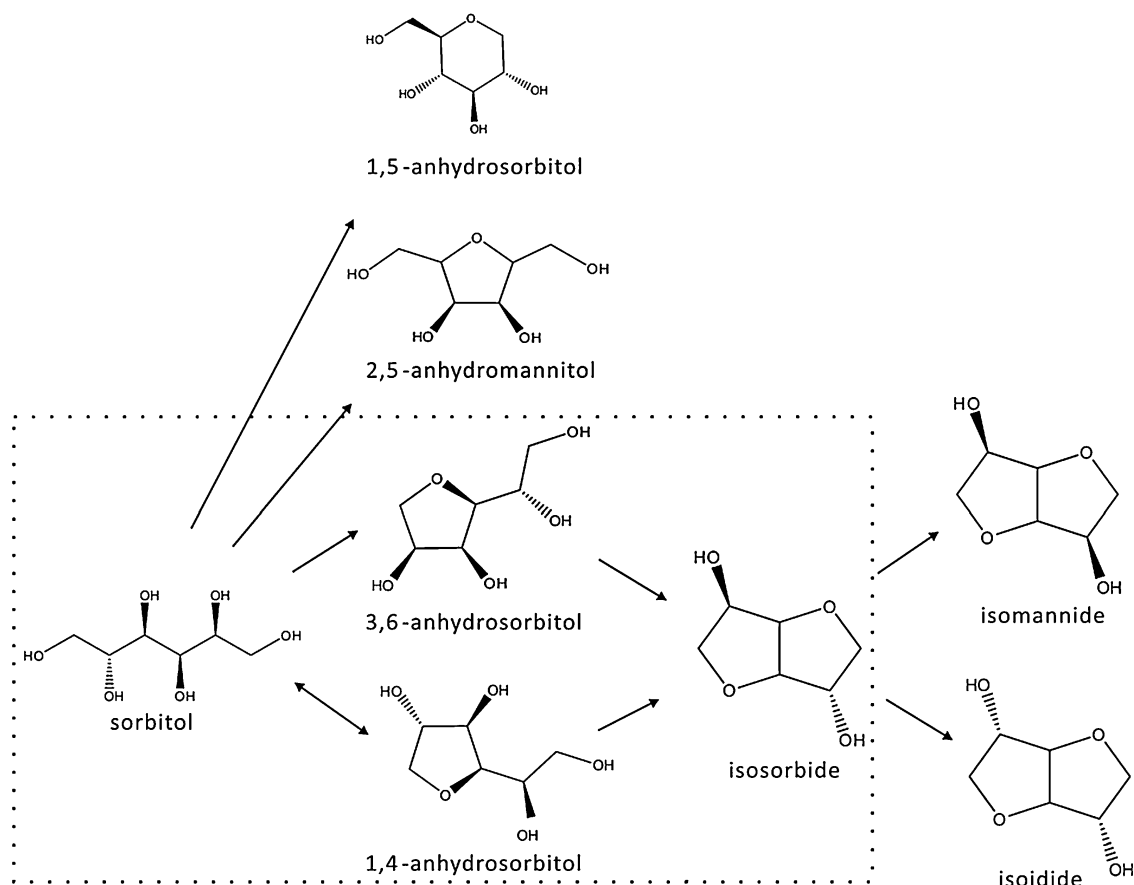


Fig. 4. Sorbitan 1,4 (MAH V) selectivity, % mol (a); MAH I and MAH II selectivities, % mol (b); MAH IV selectivity, % mol (c); P1 selectivity, % mol (d).



Scheme 1. Reaction pathway of metal phosphate catalyzed dehydration of sorbitol under hydrothermal conditions.

caused by coke deposition resulting in metal phosphates deactivation. We did not find such a behavior for the catalysts investigated in the present paper. From the results depicted in Table 3 it became obvious that the reaction time has a great influence on the sorbitol conversion and selectivity to isosorbide. At 180 °C the reaction time needed 24 h for a conversion of 96.4%, but increasing the temperature only by 10 °C–190 °C, the conversion of sorbitol is 98% already after 12 h. At 250 °C a nearly complete conversion of sorbitol (99.3%) is reached after 0.5 h. At temperatures lower than 220 °C the rate of isosorbide production in an aqueous sorbitol solution is very slow compared with higher temperatures; at 220 °C 24 h are needed to achieve 75.6% selectivity. The maximum selectivity of 80.3% is reached at 250 °C after 8 h.

We have extended this study to 270 °C and 290 °C. Temperatures higher than 250 °C and long reaction times decrease the isosorbide potential and favor the polymerization. 250 °C seems to be the optimal temperature for aqueous sorbitol solution. Thereby a maximum yield of 79.9% on a molar basis is reached after an optimal reaction time of 8 h. A quite similar yield has been reported by Ahmed et al. [21] in presence of sulfated titania at 21 °C and 0.3 bar. The problem for the catalyst involved could be the cost of synthesis compared with our simply prepared BP catalyst. When sorbitol conversion was studied using ZnCl₂ hydrate medium (70 wt.% in water) in a batch titanium autoclave pressurized until 30 bar with N₂, a higher yield of 85.5% has been reported at 200 °C [4]. It was reported that degradation of isosorbide by increased temperature can play a crucial role in the reaction [4].

All the experiments described above were carried out using 25 ml aqueous 70 wt.% sorbitol solution. We choose this volume after testing the reaction using 50 ml aqueous solution 70 wt.% sorbitol, as well. The catalytic performance (sorbitol conversion and

isosorbide selectivity) is not very different at lower reaction times (0.5–2 h); only for longer reaction times (8 h) the isosorbide selectivity was better (32.5% vs 23.3%) using the lower volume of sorbitol solution i.e., 25 ml aqueous solution 70 wt.% sorbitol.

We tried to find out if more severe conditions i.e., increasing the pressure would influence the reaction. The autoclave was flushed and pressurized to 20 bars with nitrogen before the heating was switched on. No change of the results has been observed at 200 °C.

3.2.3. Effect of acidity

The sorbitol dehydration in water at high temperature was performed in a blank test at 250 °C for 2 h. The conditions were similar with those used by Yamaguchi et al. [29]. The difference was in the batch reactor volume and material (we used 75 ml stainless steel autoclave, and the Japanese group used a batch reactor with the inner volume of 6 cm³, made of a SUS316 tube). We obtained 74.6% sorbitol conversion, 13.8% isosorbide selectivity and 57.3% 1,4 sorbitan selectivity after 2 h; the Japanese group achieved a similar conversion of sorbitol after 7 h and a maximum of 69% of 1,4 sorbitan selectivity and 15% of isosorbide after 24 h.

The tests conducted by Yamaguchi et al. in water at high temperature indicated that hydroxyl groups of isosorbide are protonated by the water molecules [29]. The decrease of the pH from 5 to 3 during our tests indicates that high concentrations of protons are generated by self-ionization of water molecules under the chosen hydrothermal conditions [43]. That means the dehydration of sorbitol to isosorbide could be affected by the proton concentration. So, we decided to add to this medium a solid acid catalyst such as BP.

The addition of BP in the batch reactor had a great influence on the reaction rate: the conversion enhanced from 74.6% to 100% and

Table 3

The influence of the temperature and of the reaction time on catalytic performance of BP in aqueous 70 wt.% sorbitol solution.

Example	Temperature (°C)	Reaction time (h)	Sorbitol conversion (% mol)	Isosorbide selectivity, (% mol)	1,4 sorbitan selectivity (% mol)	Isosorbide potential sel. (% mol)	MAHs selectivities, (% mol)
2	150	2	4.7	0	71.2	71.2	14.3
3	180	0.5	14.8	0	73.5	73.5	21.7
4	180	1	11.7	0	74.3	74.3	20.3
5	180	2	35	3.3	65.5	68.8	18.8
6	180	8	77.9	11.7	67.4	79.1	20.4
7	180	12	85	13.9	67.1	81	17.8
8	180	24	96.4	22.2	57.2	79.4	15.8
9	190	2	61.7	7.4	63.6	71	19.5
10	190	8	93.3	19.5	59.7	79.2	17.7
11	190	12	98	28.6	51.7	80.3	17.8
12	190	24	99	37.3	42.2	79.5	16.9
13	200	0.5	31.8	3.8	70.3	74.1	23.5
14	200	1	47.4	6.1	69.1	75.2	23.2
1	200	2	82.4	14.3	63.9	78.2	20.6
15	200	8	98.6	32.5	46.7	79.2	18.6
16	200	12	99.1	39.9	39.7	79.6	18.6
17	200	24	99.5	53.9	25.9	79.8	18.4
18	220	0.5	75.2	12.2	63.1	75.3	23
19	220	1	88.3	17.4	59.1	76.5	21.9
20	220	2	96.9	25.9	51.5	77.4	20.2
21	220	8	99.7	58.9	18.1	77	19.5
22	220	12	99.6	64	11.5	75.5	18.2
23	220	24	100	75.6	4.7	80.3	16.8
24 ^a	250	2	74.6	13.8	57.3	71.1	28.7
25	250	0.5	99.3	42.2	33	75.2	23
26	250	1	100	56.2	18.9	75.1	21.9
27	250	2	100	70.3	6.3	76.6	22.3
28	250	8	99.5	80.3	1.1	81.4	13.9

Conditions: BP catalyst (0.23 g); 25 ml aqueous 70 wt.% sorbitol solution; autogenous pressure: 1–30 bars; 1100 rpm. MAHs – monoanhydrohexitols.

^a Blank test.

the isosorbide selectivity from 13.8% to 70.3% after 2 h at 250 °C (see Table 3). Savage et al. [44,45] reported that the proton concentration in water at 250 °C does not affect the hydrolysis rates of organic compounds in the pH range 4–7. The pH range of sorbitol dehydration, with and without carbon dioxide, in the study of Yamaguchi et al., was estimated to be 3.5 and 6.0 respectively [29]. In this range Savage et al. [44,45] reported that water molecules mainly caused the acid-catalyzed reaction. In our study, without the BP catalyst the measured pH values varied from 5 at the beginning of the reaction to 3 at the end of the reaction. Thus we hardly could consider that we worked in the pH range of Savage. However, by adding BP the situation changed. With BP the pH range decreased drastically, from 3 at the beginning of the reaction to 1 at the end of the reaction.

We studied the influence of adding solids of different acidities. Metal phosphates (tri- and quadivalent): AlP, ZrP-1, ZrP-2, FeP, LaP, CeP, have been studied at 200 °C. The results as depicted in Table 4 were compared with a test carried out in water at high temperature without catalyst. The activity of the metal phosphates, indicated by the conversion of sorbitol, increases as follows: AlP < ZrP-1 < ZrP-2 < FeP < LaP < CeP < BP. The same order is recorded also for the selectivity to isosorbide. Analyzing the catalytic performances recorded in Table 4 with the NH₃-TPD measurements (Fig. 2) it could be concluded that the coexistence of both, strong and moderate acid sites, as in the case of BP, favor the dehydration. But as well known the acidity might be not the only parameter influencing the catalytic performance. Thus, in addition the larger average pore radius of BP compared with the other investigated phosphates (see Table 2) contribute to the better performance. In

contrast the size of the BET surface area does not influence the catalytic performance so much.

BP, with the highest activity, has a wide range of acidic strength, and all the kind of acid centers: moderate, strong and very strong. CeP, which presents only strong acid centers (nor moderate, and neither very strong) has a good activity too, but lower than that of BP. The variation of the strong acidity in the case of CeP and FeP (CeP > FeP) might account for the different catalytic activities, resulting in a better catalytic performance of CeP than over FeP. On the other hand, the excessively strong acid sites of FeP could influence its activity by deactivation. Both zirconium phosphates, with very strong (ammonia desorbed at temperatures higher than 600 °C) and excessively strong acid sites (ammonia desorbed at temperatures higher than 800 °C) show minor catalytic performance. AlP, which has a very low acidity, results in low catalytic activity, as well. From these results one could conclude that sorbitol dehydration is favored by moderate and strong acid sites, and not favored by very strong and excessively strong acidity.

Looking at the values found with the nitrogen adsorption no rule can be drawn out of these data. The boron phosphate has one of the smallest surface areas, nevertheless one of the highest activity and the best selectivity. The reason for that seems to be the highest pore radius. Furthermore, FeP, with the highest BET area, has a low activity (again this could be explained by its acidity). The higher BET surface area (16 vs 4 m²/g) and the higher average pore radius (107.8 Å vs 63.2 Å) of ZrP-2, comparing with ZrP-1, seems to compensate the fact that it has only excessively strong acid centers (which normally are deactivated by time, but a higher pore radius could decrease the rate of deactivation) and resulted in a

Table 4

Catalytic performances of metal phosphate catalysts in sorbitol dehydration of an aqueous 70 wt.% sorbitol solution.

Catalyst	Sorbitol conversion (% mol)	Isosorbide selectivity (% mol)	1,4 sorbitan selectivity (% mol)	Isosorbide potential selectivities (% mol)	pH range (pH _i –pH _f)
–	3.1	0	49	49	5–4
AlP	3.5	0	76.9	76.9	5–4
ZrP-1	9.2	0	74.1	74.1	4–3
ZrP-2	21.4	2.8	71.8	74.6	–3
FeP	29.6	4.2	68	72.2	5–3
LaP	57.3	8.5	68.7	77.2	2–2(3)
CeP	60.1	9	68.7	77.7	3–3(4)
BP	82.4	14.3	63.9	78.2	3–1

Conditions: 0.23 g of catalyst; temperature: 200 °C, time on reaction (TOS): 2 h, autogenous pressure: 1–14 bars, $V_{\text{reaction}} = 25$ ml aqueous 70 wt.% sorbitol solution; 1100 rpm.

better catalytic activity. The conclusion is that BET surface area, the pore radius and the acidity should be considered as three combined parameters. Also, we believe that high temperature liquid water has a great influence on sorbitol dehydration, too.

We tried to find similar correlations between the catalytic performances and the pH range of the reactions medium (Table 4). In the case of AlP, at the pH > 4, we can assume that water molecules mainly caused the dehydration of sorbitol [43,44,45]. The presence of AlP changed only the selectivity to 1,4 sorbitan. It is known that Lewis centers mainly lead to 1,4 sorbitan [10]. ZrP-1, ZrP-2, FeP as well as CeP created a pH medium (pH 3–4) with a value somehow at the limit of the range proposed by Savage et al. [44,45]. That could mean the reaction is caused by water molecules and by acid centers of the solids, as well. But we can assume that the water molecules can affect also the acidities of the solids, so there is not a very good idea to interpret the results only from the point of view of the solid acidities. This will be better explained in the next section. It is obvious that in the case of LaP and BP (pH 1–3) the acidity of the solid has a great influence on the reaction of dehydration of sorbitol.

The combination of all these factors (solid acidity, surface area, average pore radius and pH) as well as the conditions used, atmospheric pressure vs hydrothermal pressure vs pressurization, could be a reason for all the discrepancies found in the literature when one correlates the catalytic performance of a catalyst in dehydration of sorbitol only with its acidity. Thus, Patel et al. [46,47] referred the variation of the catalytic activity of tetravalent tin phosphate, zirconium phosphate and titanium phosphate on cyclodehydration of 1, *n*-diols on the basis of their total number of acid sites and of their number of strong acid sites, as well as of their surface area. In contrast, Xia et al. have found out that the weaker the acid strength of sulfated metal oxides, the higher their activity in sorbitol dehydration to isosorbide (they used atmospheric pressure and 10% aqueous sorbitol solution) [48]. Using the same conditions as above, Tang et al. have reported that the moderate strong acid sites of phosphated Nb₂O₅ catalyzed more effectively the reaction [49].

As Savage et al. claimed that acid catalyzed reactions (in high temperature liquid water at 200 °C–300 °C) could proceed not only by protons but also by water molecules [43–45], we tried to find more about the influence of water molecules on the catalysts performances in sorbitol dehydration in the next section.

3.2.4. Effect of catalyst pretreatment

Freidlin et al. [50] found that the activity per unit surface area of boron phosphate in dehydration processes increases with pretreatment temperature and passes through a maximum at 600 °C. This motivates us to study the influence of the catalyst pretreatment for the desired reaction. The catalytic performance of BP, ZrP and CeP after different pretreatments has been shown in Table 5.

There is not a general rule that we could design concerning the behavior of the calcined BP compared with the uncalcined BP (compare examples in Table 5 with examples in Table 3). It can be assumed, from the variation of pH (pH_i–pH_f 5–1), that at the begin-

ning of the reaction water molecules of the reaction medium play an important role, and by time, the catalyst acidities influence the reaction as well [43–45].

After 2 h at 200 °C, the results of BP⁴⁰⁰ and BP⁶⁰⁰ are identical with those of BP uncalcined. At temperatures lower than 200 °C (180 °C) BP²⁰⁰ presents lower activity than BP (Examples 29, 30/Table 5 vs Examples 5, 8/Table 3), while BP⁶⁰⁰ yields better activity than BP. A big difference is noticed after 2 h. The 1,4 sorbitan selectivity obtained over BP²⁰⁰ is very low (24.7%) compared with 65.5% in the case of BP. After 24 h of reaction the isosorbide potentials of both catalysts are quite similar. BP²⁰⁰ has a slightly decreased isosorbide selectivity compared with BP. In contrast, BP⁶⁰⁰ shows a higher activity than BP in the first 2 h and identical selectivity to isosorbide and 1,4 sorbitan as BP. Interestingly, after 24 h both catalysts, BP⁶⁰⁰ and BP have the same performances in terms of activity and selectivities.

At 220 °C, BP²⁰⁰ and BP⁶⁰⁰ present similar catalytic performances. Both of them show the same sorbitol conversion as BP, but higher isosorbide selectivity in the first 2 h. After 24 h the isosorbide selectivity are quite similar, but slightly decreased in the case of BP²⁰⁰. These results can be hardly correlated with the characteristics of the catalysts. The big challenge remains the interpretation of the results taking into account the acidity of the solids. It is very curious that BP²⁰⁰, which is not very different from BP in terms of strength acidity, as the TPD measurements indicate, has a different catalytic behavior at 180 °C. In contrast, BP⁶⁰⁰, which is very different than BP (the moderate and the strong acid sites disappeared during calcination and it shows only excessively strong acid sites), presents similar behavior as BP at 200 °C.

The existence of both Lewis and Brönsted acid sites on boron phosphorous oxides was reported, but when P/B ratio is >1 (as 1.2 in our case) the acid sites are predominantly of the Brönsted type [37]. It was proven that in the case of boron phosphate the P–OH and B–OH centers are reduced with increasing pretreatment/calcination temperature but afterwards are regenerated to a large extent when exposed to water vapor [51]. It can be also concluded in our case that the number of such Brönsted type centers are regenerated in the aqueous reaction mixture. That means the moderate and strong acid sites disappear during calcination at 400 °C and 600 °C. Those are reactivated by contact with water of the reaction medium.

The active centers reactivation seems to be influenced by the reaction temperature. The identical results obtained with BP⁴⁰⁰ and BP⁶⁰⁰ as well as BP at 200 °C conclude that such a temperature is sufficient to obtain a similar distribution of the active centers as that of BP. The same results obtained at 220 °C over both BP²⁰⁰ and BP⁶⁰⁰ made us to believe that at this temperature both catalysts have similar distribution of the reactivated active centers, but different than that of BP. A different distribution of the reactivated acid centers than that of BP is obtained at 180 °C, too. Furthermore, a calcination temperature of 200 °C is not sufficient for water inclosed in the bulk to remove during calcination and some pores are blocked [31] (S_{BET} decreases). This fact could explain the lower activity of

Table 5

The influence of temperature and reaction time on the performance of calcined metal phosphates in aqueous 70 wt.% sorbitol solution.

Example	Catalyst	Temperature (°C)	Reaction time (h)	Sorbitol conversion (% mol)	Isosorbide selectivity (% mol)	1,4-sorbitan selectivity (% mol)	Isosorbide potential selectivities (% mol)	pH _i –pH _f
29	BP ²⁰⁰	180	2	24.7	2.5	24.7	27.2	–
30	BP ²⁰⁰	180	24	89.6	15.5	66.4	81.9	–
31	BP ²⁰⁰	220	2	98.7	33.3	43.4	76.7	–
32	BP ²⁰⁰	220	24	100	70.5	8.6	79.1	–
33	BP ⁴⁰⁰	200	2	83.7	14.5	63.7	78.2	5–1
34	BP ⁶⁰⁰	180	2	41.3	4	67.1	71.1	5–1
35	BP ⁶⁰⁰	180	8	77.4	11	66.6	77.6	5–1
36	BP ⁶⁰⁰	180	12	84.4	11	59.6	70.6	5–1
37	BP ⁶⁰⁰	180	24	94.9	19.1	60.9	80	5–1
38	BP ⁶⁰⁰	200	2	81.1	14.1	63.9	78	5–1
39	BP ⁶⁰⁰	220	2	98.6	34.3	42.8	77.1	5–1
40	BP ⁶⁰⁰	220	24	100	72.3	7.2	79.5	5–1
41	ZrP ₁ ⁴⁰⁰	200	2	8.8	0	74.7	74.7	5–4
42	ZrP ₂ ⁴⁰⁰	200	2	17.8	0	74.8	74.8	5–4
43	ZrP ₂ ⁶⁰⁰	200	2	11.1	0	73.8	73.8	5–3(4)
44	CeP ⁶⁰⁰	200	2	57.3	7.9	68.9	76.8	5–1(2)

Conditions: V_{reaction} = 25 ml aq. 70 wt.% sorbitol solution; catalyst 0.23 g.

BP²⁰⁰ compared with BP at 180 °C. It looks like that 180 °C are not sufficient to increase the mobility of blocked water molecules.

It is interesting that differences between the performances of the calcined BP and BP itself occur in the first 2 h. After 24 h the results of the calcined form are quite similar with those obtained by BP uncalcined. As the initial pH (pH_i) increased in the case of the calcined form of BP to 5, that could mean that in the first step of the dehydration of sorbitol water molecules are involved in regeneration of the active centers and in the reaction as proton donors, as well [43–45]. With time, by regeneration, the acidities of the calcined solids become similar with that of BP uncalcined, and thus, the activities are similar.

Yamaguchi et al. [29] concluded that at high temperature the protonation by water molecules is not a rate-determining step, and that the other steps of dehydration as the attack of an O atom (of a hydroxyl group) at a C atom with –OH₂⁺ and the simultaneous elimination of water are the rate-determining (SN2 mechanism). Furthermore, by kinetic studies they found out that the rate formation of 1,4 sorbitan is higher than that of isosorbide, as the protonation of sorbitol proceeds preferentially at both the C1 and C6 positions. This could explain the great influence of the reaction temperature on our results. Thus, by increasing the water mobility are enhanced the probabilities as two water molecules hint the sorbitol molecule in the 2 preferentially positions. Furthermore, the formation of the bulky structure of the intermediate of the mechanism proposed is favored by the more confined spaced offered by the solids pores.

Comparing the performance of ZrP-1, ZrP-2 and CeP before (Table 4 and Table 5) and after calcination treatment it is realized that after calcination the catalytic activity of these phosphates is slightly decreased. It is reported that the surface area of zirconium phosphate increases with calcination temperature [52]. The gradually decrease in activity of both ZrP-1 and ZrP-2 by calcination at 400 °C could be explained by the gradually increase of the strong acidity during the thermal treatment up to 400 °C. The abruptly decrease in activity of ZrP-2 by calcination at 600 °C could be explained by the abruptly decrease of the total acidity when the temperature treatment is higher than 450 °C, as reported [53,54].

3.2.5. Effect of sorbitol concentration

Sorbitol dehydration behavior was investigated using different initial sorbitol concentrations (70 wt.% and 100 wt.%) at 200 °C. The results are presented in Table 6. A sorbitol conversion of 100% is reached already after 1 h reaction time using 100% sorbitol powder compared with 96.5% sorbitol conversion attained after 8 h using aqueous 70 wt.% sorbitol solution. The rate of isosorbide formation

from molten sorbitol is considerably increased. After 8 h the isosorbide selectivity is 52.6% using 100% sorbitol powder compared with 23.3% selectivity in case of the 70 wt.% sorbitol solution as reactant.

We have extended the study of molten sorbitol dehydration to higher temperatures, 220 °C, 250 °C, 270 °C and 290 °C. After 2 h reaction time at 220 °C we achieved a sorbitol conversion of 99.5%, a isosorbide selectivity of 40.5% and a 1,4 sorbitan selectivity of 36%. The isosorbide selectivity increased to 75.5% and 1,4 sorbitan selectivity decreased to 3.1% after 8 h reaction time. Temperatures higher than 220 °C and long reaction times decrease the isosorbide potential and favor the polymerization that means deactivation of the catalyst occurs. That happened with a very low rate in 70 wt.% aqueous sorbitol solution only at temperatures higher than 250 °C. Very good results concerning the isosorbide potential and selectivity were achieved when sorbitol powder was heated up to 180 °C for 2 h and afterwards the temperature was increased to 250 °C for another 2 h (the results are not reported here).

220 °C seems to be the optimal temperature for molten sorbitol conversion to isosorbide with a maximum yield of 75.5% on a molar basis at an optimal reaction time of 8 h, and 250 °C for aqueous sorbitol solution, when a maximal percent yield of 79.9% on a molar basis at an optimal reaction time of 8 h is reached.

All the tests above were performed with 45.5 g 100% sorbitol powder filling the autoclave volume and 0.46 g of BP. When the autoclave was filled with 32.3 g of sorbitol powder (0.326 g of BP) and the reaction was carried out at 200 °C for 2 h the conversion of sorbitol increased from 97.9% to 100% and isosorbide selectivity increased from 26.9 to 57.3%. It seems that a larger free reaction volume is in favor for the reaction.

3.2.6. Depressurizing the autoclaves

Some experiments were carried out in order to prove the influence of reduced pressure on the equilibrium shift. When the temperature of the reaction mixture reached the desired value (reaction time considered $t=0$) the autoclave was depressurized within 10–15 s (until no steam came out from the autoclave).

Checking the evolution of the selectivity to isosorbide over BP in the first two h of the reaction, at 200 °C, it was noticed that the efficiency of the reaction raised by equilibrium shift. The problem was that after depressurizing the autoclave the temperature fluctuated between ± 35 °C from 200 °C. It is shown that the displacement of the reaction equilibrium is in favor for the formation of isosorbide because after 0.5 h 97.1% conversion of sorbitol and 38.7% selectivity to isosorbide are obtained. Complete conversion and 73% selectivity to isosorbide are achieved already after 1 h at 200 °C. In addition around 6% 1,4 - sorbitan was found (78.7% isosorbide

Table 6

The catalytic performances of BP on dehydration of sorbitol using aqueous 70 wt.% sorbitol solution and sorbitol 100 wt.% as starting material.

Example	Reaction time (h)	Sorbitol conversion (% mol)	Isosorbide selectivity (% mol)	1,4 sorbitan selectivity (% mol)	Isosorbide potential selectivities (% mol)	MAHs selectivity (% mol)
Aqueous 70 wt.% sorbitol solution ^a						
45	0.5	30.2	3.5	70.1	73.6	23.2
46	1	43.7	5.4	69.9	75.3	22.5
47	2	78.8	12.7	64.7	77.4	21.4
48	8	96.5	23.3	56.1	79.4	18.6
Sorbitol 100 wt.% ^b						
49	0.5	91.1	18.5	57.3	75.8	23.2
50	1	100	22.5	54.3	76.8	22.2
51	2	97.9	26.9	50.4	77.3	21.7
52	8	100	52.6	24	76.6	20.8

Conditions: 200 °C, 0.46 g of catalyst.

^a V_{reaction} = 50 ml aqueous 70 wt.% sorbitol solution.^b 45.5 g of sorbitol powder; MAHs – monoanhydrohexitols.

potential selectivities). After 2 h of reaction the sorbitol conversion decreased to 98.5% and the isosorbide selectivity to 33.4% (76.3% isosorbide potential selectivities). But during depressurization the vapors of water coming out of the autoclave were mixed with some sorbitol. So, the depressurization is of benefit but it has to be exactly controlled.

4. Conclusions

Sorbitol dehydration under hydrothermal conditions at 180–250 °C, using aqueous 70 wt.% sorbitol solution and molten sorbitol as reaction medium, proceeded with and without Me(III)- and Me(IV)-phosphates as catalysts. The dehydration of sorbitol proceeded via two steps. In the first dehydration step two types of monoanhydrosorbitols are formed; the first type (1,4- and 3,6-anhydrosorbitol) reacts sequentially to isosorbide and the second type (1,5- and 2,5- anhydrosorbitol) is stable towards further dehydration.

The blank test performed at 250 °C for 2 h gave 74.6% sorbitol conversion, 13.8% isosorbide selectivity and 57.3% 1,4 sorbitan selectivity. The presence of the heterogeneous catalyst acid BP in the batch reactor had a great influence on the reaction rate: the conversion enhanced to 100% and the isosorbide selectivity to 70.3%, whereas 1,4 sorbitan selectivity is reduced to 6.3%. The acidities of BP and LaP have a great influence on the reaction. When ZrP-1, ZrP-2, FeP and CeP are used as catalysts the conversion is caused by water molecules and by acid centers of the solids, as well. In the case of AlP we assume that water molecules mainly caused the dehydration of sorbitol. The activity of the metal phosphates, indicated by the conversion of sorbitol increases as follows: AlP < ZrP-1 < ZrP-2 < FeP < LaP < CeP < BP. The same order is recorded also for the selectivity to isosorbide. Sorbitol dehydration is favored by moderate and strong acid sites, and not favored by very strong and excessively strong acidity. In addition the large average pore size contributes to the good catalytic performance of the BP catalyst.

The temperature and the reaction time influence strongly the catalytic performance. A pressure of 20 bars prior to the reaction does not affect the performance of BP catalyst. The optimal conditions for BP in a 70 wt.% aqueous sorbitol solution are 250 °C for 8 h resulting in 79.9 mol% yield). Molten sorbitol was dehydrated with a higher reaction rate than aqueous 70 wt.% sorbitol solution. The optimal conditions for BP are 220 °C for 8 h achieving 75.5 mol% yield.

The acid centers strength distribution of BP changes by calcination at 400 °C and 600 °C; the moderate and strong acid sites disappear and excessively strong acid sites are formed. By contact with water of the reaction medium the active centers are reactivated. The reactivation of the active centers occurs in the first 2 h of reaction when water molecules are involved in regeneration of

the active centers and in the reaction as proton donors, as well. Thus, differences between the performances of the calcined BP and BP itself occur in the first 2 h of reaction. The new distribution of the active centers depends on the water temperature, e.g., at 200 °C it is very similar with that before the calcination, so the same activity it shows. By calcination of both ZrP-1 and ZrP-2 at 400 °C and 600 °C the strong acidity gradually increases while the total acidity abruptly decreases. This results in decrease in activity of both ZrP-1 and ZrP-2. The reaction equilibrium shift managed by depressurizing the autoclave during the experiment is in favor for the formation of isosorbide.

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